Angular Dependence of Charge-Transfer Probabilities between O^- and a Ni{100}-$c(2\times2)$-O Surface

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The negative-ion fractions of oxygen directly recoiled from a Ni{100}-$c(2\times2)$-O surface have been measured as a function of both azimuthal and exit angles. The data show a pronounced angular dependence of the ion fractions. A theoretical analysis suggests that the probability for charge transfer between an oxygen atom and the surface varies strongly with lateral position. The experiments provide a 3D map of the local electron tunneling rates within the surface unit cell.

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The energies and lifetimes of excited states of atoms and molecules at or near metal surfaces are controlling factors in many dynamical phenomena. For example, electrons or photons can stimulate desorption of surface atoms if electronically excited repulsive states are localized and sufficiently long lived [1]. The angular, velocity, charge, and electronic state distributions of sputtered and scattered particles depend strongly on the lifetimes of the electronic states [2,3]. In the spectroscopy of adsorbed species, the lifetimes of excited states contribute to the broadening of adsorption peaks [4]. In the conventional interpretation of charge-transfer data between atoms and surfaces, it is assumed that charge transfer occurs at such large distances that the surface structure is not a significant perturbation [5]. Recently, several groups have performed experiments on impurity-covered surfaces and concluded that the lateral corrugation of the surface potential must be included for proper interpretation of the data [6-8]. Theoretical studies have subsequently verified that both the tunneling rates and energy shifts can be strongly influenced locally by impurities coadsorbed on a surface [9].

In this Letter, a detailed investigation of the negative-ion fraction of oxygen directly recoiled from a Ni{100}-$c(2\times2)$-O surface is presented. The data show a strong angular dependence of the charge-transfer probabilities between an atom and the surface. These measurements, combined with a theoretical model for charge transfer, provide a detailed microscopic map of the local electron tunneling rates between an individual atom and the surface. This information is similar to that obtained using scanning tunneling microscopy but of more direct relevance for the microscopic understanding of the reactivity of surfaces.

Although of fundamental importance for the understanding of catalytic promotion and poisoning phenomena [10], relatively little has been learned about the spatial dependence of atom-surface tunneling rates from ion-surface scattering experiments. The reason for this is that the lateral dependence of charge-transfer probabilities is difficult to measure directly using ion-surface scattering techniques since the width of the ion beam is always much larger than the dimension of a surface unit cell. A direct method for studying the spatial dependence of charge-transfer probabilities at keV energies within the surface unit cell is developed herein using the direct recoiling method of the technique of time-of-flight scattering and recoiling spectrometry (TOF-SARS) [11]. Charge transfer at keV energies is not necessarily representative of stimulated desorption, catalysis, or other low-energy processes.

A detailed description of the TOF-SARS technique has been presented elsewhere [11]. The Ni{100} surface was cleaned [12] by cycles of sputtering and annealing. A sharp $c(2\times2)$-O LEED pattern was obtained after room-temperature exposure to 60 langmuirs of O_2. The $c(2\times2)$-O structure has been thoroughly studied [12] and it is now well accepted that the oxygen atoms are in fourfold hollow sites and about 0.9 Å above the outermost Ni layer. The operating conditions for these experiments are as follows: 4-keV Ar^+ pulsed primary beam, 50-ns pulse width, 0.5-nA/cm^2 ion current, 50-kHz pulse rate, $\phi=41°$ recoil angle, channel electron multiplier detector with cone grounded. The recoiled O^- ion fractions were determined by collecting the TOF spectra of neutrals (N) and ions (I) simultaneously using an acceleration lens to temporally separate the N and I particles [12]. Ion fractions were calculated as $Y=I/(N+I)$ with an error of $<\pm2\%$. Using different acceleration voltages, it was determined that most of the ions were O^-; the ion fraction of positive and doubly charged negative oxygen ions was $<1\%$. Oxygen atoms that are directly recoiled [13] into $\phi=41°$ by 4-keV Ar^+ have an energy of ≈1.86 keV; in this energy range, the detector response to both N and I particles is similar [13].

The O^- ion fractions were collected as a function of the Ar^+ beam incident angle to the surface (α) and the crystal azimuthal angle (δ). The angle between the oxygen recoiling trajectory and the surface is $\beta=41°-\alpha$. The results are plotted in Fig. 1 as a three-dimensional surface in (β,δ) space. Approximately 3 h of collection time was required to obtain the data in Fig. 1 with good

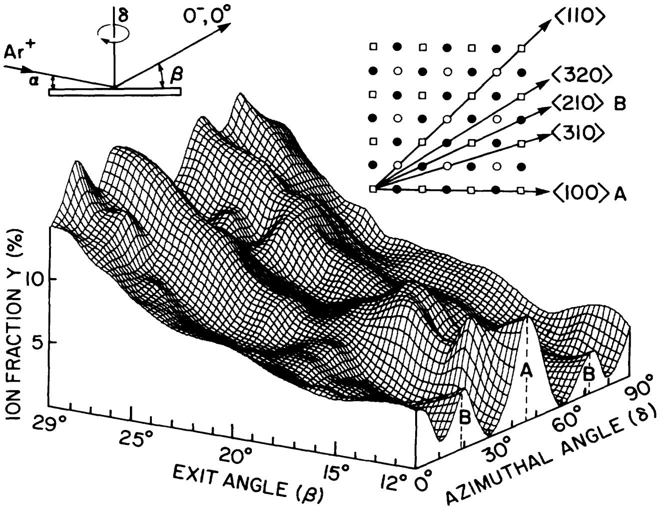

FIG. 1. Recoiling O^- ion fraction plot for the Ni{100}-$c(2\times2)$-O surface using 4-keV Ar^+ ions and $\phi=41°$. The O^- ion fractions are plotted as a function of exit β and azimuthal δ angles.

statistics. In order to avoid ion-beam-induced effects on the surface structure, the sample was reannealed and redosed with O_2 after ion doses of 10^{13} ions/cm^2, i.e., $\approx 10^{-2}$ ion/surface atom. The Y values follow the general trend of increasing as the ion velocity perpendicular to the surface increases, varying from (2–10)% at low β up to (13–18)% at high β. The observed features indicate maxima and minima along various principal azimuths that are symmetrical about the ⟨100⟩ direction. Note that at the extreme β values used, i.e., $\beta=11°$ and 29°, the maxima and minima along the various azimuths are exactly reversed. At low β the maxima are along the ⟨100⟩, ⟨210⟩, and ⟨110⟩ azimuths while the minima are along the ⟨310⟩ and ⟨320⟩ azimuths; these are reversed at high β. This lateral and vertical dependence of the ion fractions indicates that the charge-transfer mechanism between an oxygen atom and the surface is sensitive to atomic structure.

The probability of charge transfer between an atom and a metal surface depends both on the relative position of the atomic level with respect to the Fermi energy and on the tunneling rates between the atomic state and the surface. A first-principles calculation of the energy shift and broadening of atomic states outside a Ni{100}-$c(2\times2)$-O surface would be impossible with present resources. A qualitative description and understanding of the experimental result can, however, be obtained from a simple model.

The starting point is the result from a recent calculation using the complex scaling method [14] for the energy shift and broadening of atomic negative-ion states as a function of distance outside a jellium surface [15]. The energy of the triply degenerate $O^-(^2P)$ state shifts downwards as the surface is approached, closely following the bare surface potential. The full widths of the O^- levels outside a Ni surface can be parametrized as $\Gamma_0(Z)=3.4\exp(-0.60Z)$ for the $m=0$ level and $\Gamma_{\pm1}(Z)=1.0\exp(-0.68Z)$ (in eV) for the $m=\pm1$ levels [15], where Z is the distance from the Ni surface. The two $m=\pm1$ states oriented parallel to the surface have lifetimes that are about 1 order of magnitude longer than that of the $m=0$ state [16]. This fact has important consequences for the formation and survival of the negative ion. At positions close to the surface, all oxygen neutral states are shifted up and negative-ion states are shifted down in energy. Any collisionally induced neutral excitation will therefore decay immediately with the instantaneous formation of negative states. Since the width of the $m=0$ state is much broader than that of the $m=\pm1$ state and since transition probability is proportional to width, the $m=0$ state will be formed with much higher probability than the $m=\pm1$ state.

The qualitative features of the ion-fraction recoil map in Fig. 1 can be accounted for by simply calculating the survival rate of the $m=0$ state recoiled from a homogeneous metal surface. The small fraction of $m=\pm1$ states formed near the surface survive the outgoing trajectory even at grazing exit angles. However, Fig. 1 shows an important structure which gives evidence for a lateral corrugation of the charge-transfer probabilities. It will be shown that this structure can be understood from general arguments derived from a simple chemisorption study of oxygen on metal surfaces.

The chemisorbed oxygen layer alters the electronic properties of the surface; in particular, there is an oxygen-induced change in the surface potential. The chemisorption of oxygen on metal surfaces has been studied self-consistently using local-density methods [17,18]. At normal distances above the chemisorbed oxygen, the induced one-electron potential ΔV_0 is positive, reflecting the fact that the oxygen atom is electronegative and induces a weak dipole potential in the surface region.

The inhomogeneity introduced by the oxygen overlayer will induce a lateral corrugation of the surface potential. A simple estimate of this effect can be obtained by linear superposition of the individual oxygen-induced potentials,

$$\Delta V(\mathbf{r})=\sum_{\mathbf{R}_0}\Delta V_0(\mathbf{r}-\mathbf{R}_0)\,, \tag{1}$$

where the sum is over all chemisorbed oxygen atoms. The oxygen overlayer will induce a lateral corrugation of the negative-ion level of the recoiled oxygen,

$$\epsilon_m(\mathbf{R})=\epsilon_m^0(Z)+\Delta\epsilon_m(\mathbf{R})\,, \tag{2}$$

where $\epsilon_m^0(Z)$ is the calculated energy shift at a distance Z from a jellium surface. To lowest order, the energy shift of the atomic level near an impurity will follow the local electron potential [9],

$$\Delta\epsilon_m(\mathbf{R})=\Delta V(\mathbf{R})\,. \tag{3}$$

In Fig. 2, the lateral variation of the negative-ion state is shown at a distance of 3.5 a.u. from the oxygen layer. It can clearly be seen that the affinity level of the recoiled

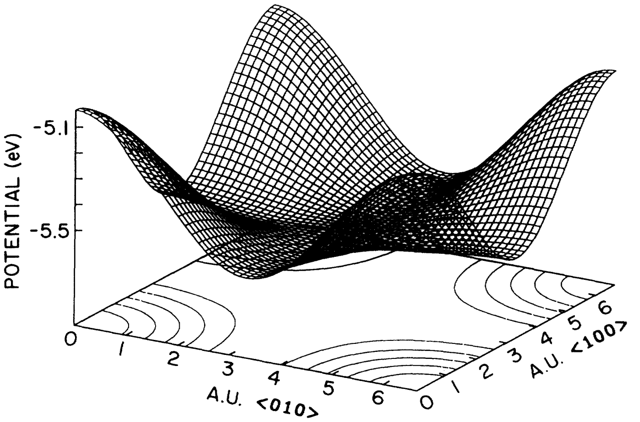

FIG. 2. Oxygen-induced electrostatic potential $V(x,y,z)$ in the surface unit cell for $Z=3.5$ a.u. The oxygen atoms are chemisorbed at $Z=-1$ a.u. and located at the four corners. The contour lines of constant potential are projected in the plane below.

oxygen shifts upwards above a chemisorbed oxygen atom. Such an upshift reduces the survival probability of the negative-ion state, since the state can depopulate closer to the surface. Oxygen ions recoiled above oxygen-rich rows will therefore neutralize more rapidly than above metal-rich rows. This effect causes a reduction in the negative-ion fraction for oxygen moving along oxygen-rich rows at steep exit angles, in agreement with the experimental observations.

At grazing exit angles, the situation is different. At $\beta=11°$, the recoiled oxygen atom initially passes very close to neighboring chemisorbed oxygen atoms. In the $\langle 100\rangle$ direction, the oxygen-oxygen distances during the first two encounters with chemisorbed oxygen atoms are 1.3 and 2.6 a.u. During these close encounters, the energies of the oxygen states will shift differently. The $m=0$ state oriented perpendicular to the surface will shift upwards when on top of a chemisorbed oxygen and back downwards when off the on-top position. The $m=\pm 1$ states are much less sensitive to the lateral position. We thus expect the atomic $m=0$ state to cross the $m=\pm 1$ states on both sides of the chemisorbed oxygen. When this happens, there is a possibility for transitions between these states. A calculation of the matrix element between the diabatic states and the surface potential shows that such transitions will occur with a finite probability. The theoretical approach is, however, not adequate for more than a qualitative description of these events. Any $O^-(^2P, m=\pm 1)$ states created during the initial part of the trajectory along grazing exits have a high survival probability. The angular dependence of the ion fraction at grazing exit is therefore opposite to the situation at steeper exits, with higher ion fractions for trajectories along oxygen-rich rows than along metal-rich rows, in agreement with the experimental data.

The charge transfer along the trajectory is calculated from the coupled equations [19]:

$$\frac{d}{dt}n_m(t) = -\Gamma_m(t)\left[[1-f_m(t)]n_m(t) - f_m(t)\left(1-\sum_{m=-1}^{1} n_m(t)\right)\right], \tag{4}$$

where $m=-1$, 0, or 1 and $f_m(t)$ is the Fermi-Dirac function $f_{\mathrm{FD}}(\epsilon_m(t))$. The probability for an $m=0$ to $m=\pm 1$ transition during a near collision between two oxygen atoms is phenomenologically taken into account by adding a term $c(t)(n_m - \sum_{j\neq m} n_j)$. The function $c(t)$ is parametrized as

$$c(t) = c_0 \exp[-(\zeta/\xi)^2]\exp[-(z/\eta)^2], \tag{5}$$

where ζ is the lateral distance between a chemisorbed oxygen and the recoiled atom. Ideally, the three parameters in this expression should be calculated. In this application, the parameters were chosen to resemble the experimental data at the exit angle of 11°, with the result $c_0=0.005$, $\xi=1.0$, and $\eta=2$. The surface work function is $\phi=5.4$ eV and the initial charge state of the oxygen is assumed to be $n_{\pm 1}=0$ and $n_0=1$. Calculation assuming that the oxygen starts as a neutral atom gives identical results.

The above equations were solved for the different azimuthal and exit angles; the resulting negative-ion fractions are plotted in Fig. 3(a). The major qualitative features discussed previously are all reproduced. The detailed agreement between the calculated negative-ion fractions and the experimental data can be improved by introduction of a more realistic but phenomenological description of the shift and broadening of the negative-ion levels near the surface [20].

The calculated recoil map using these shifts and broadenings is shown in Fig. 3(b). Figure 3(b) compares very well with the experimental data of Fig. 1. First-principles calculations of the lateral variations of the atomic level shifts and broadening outside strongly corrugated metal surfaces are in progress.

In conclusion, this paper has reported the first direct observation of a lateral dependence of the charge-transfer probabilities between an atom and a corrugated surface. The qualitative features of the experiment can be understood from simple general arguments. These types of measurements provide a detailed microscopic map of the local reactivity of the surface. This information can be of crucial importance for the understanding of various impurity-induced promotion and poisoning phenomena in catalysis and electron density maps from scanning tunneling microscopy. A paper presenting the experimental and theoretical details is presently being prepared.

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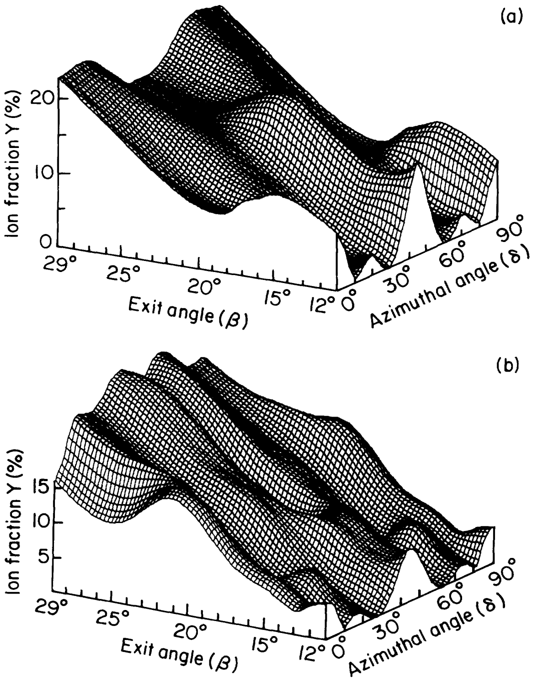

FIG. 3. Calculated negative-ion fraction as a function of exit β and azimuthal δ angles. The ion velocity and orientation of the crystal are the same as in Fig. 1. (a) Calculated using Eq. (4). (b) Calculated according to the approximations given by the equations in Ref. [20].

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[20] From first-order perturbation theory, the shifts of the negative-ion levels are $\Delta\epsilon_m(\mathbf{R}) = \int d^3r\, \psi_m(\mathbf{R}-\mathbf{r})\Delta V(\mathbf{r}) \times \psi_m(\mathbf{R}-\mathbf{r})$. The tunneling rates between the recoiling oxygen and the surface will be slightly enhanced above a chemisorbed oxygen atom. This effect can be taken into account by introducing a lateral corrugation of the widths $\Gamma_m(\mathbf{R}) = \Gamma_m(Z)[1 + A\sum_{\mathbf{R}_0}\exp(-B\rho_{\text{O-O}})]$. The negative-ion fractions calculated using these equations are shown in Fig. 3(b). The best fit to the experimental data was obtained using $A=2$ and $B=1$. This parameter choice appears reasonable [9].